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(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
15 November 2001 (15.11.2001)

PCT

(10) International Publication Number
WO 01/86353 A1

- (51) International Patent Classification⁷: **G03F 7/039**
- (21) International Application Number: PCT/US01/14914
- (22) International Filing Date: 8 May 2001 (08.05.2001)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
09/567,634 9 May 2000 (09.05.2000) US
- (63) Related by continuation (CON) or continuation-in-part (CIP) to earlier application:
US 09/567,634 (CIP)
Filed on 9 May 2001 (09.05.2001)
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- (81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.
- (84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).
- Published:**
— with international search report
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*



WO 01/86353 A1

(54) Title: POLYMERS CONTAINING OXYGEN AND SULFUR ALICYCLIC UNITS AND PHOTORESIST COMPOSITIONS COMPRISING SAME

(57) Abstract: The invention includes polymers that contain a heterocyclic ring, preferably an oxygen- or sulfur-containing ring. The heterocyclic ring is preferably fused to the polymer backbone. The invention also provides photoresists that contain such polymers, particularly for imaging at short wavelengths such as sub-200 nm.

POLYMERS CONTAINING OXYGEN AND SULFUR ALICYCLIC UNITS
PHOTORESIST COMPOSITIONS COMPRISING SAME

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to new polymers that contain oxygen and/or alicyclic (heteroalicyclic) units and use of such polymers as a resin binder component of photoresist compositions, particularly chemically-amplified positive-acting resist, be effectively imaged at short wavelengths such as sub-200 nm, particularly 193 nm.

2. Background

Photoresists are photosensitive films used for transfer of images to a substrate. A coating layer of a photoresist is formed on a substrate and the photoresist layer is exposed through a photomask to a source of activating radiation. The photomask defines areas that are opaque to activating radiation and other areas that are transparent to activating radiation. Exposure to activating radiation provides a photoinduced chemical transformation of the photoresist coating to thereby transfer the pattern of the photomask to the photoresist-coated substrate. Following exposure, the photoresist is developed to provide a relief image that permits selective processing of a substrate.

A photoresist can be either positive-acting or negative-acting. For most negative-acting photoresists, those coating layer portions that are exposed to activating radiation polymerize or crosslink in a reaction between a photoactive compound and polymer reagents of the photoresist composition. Consequently, the exposed coating portions are rendered less soluble in a developer solution than unexposed portions. For a positive-acting photoresist, exposed portions are rendered more soluble in a developer solution while areas not exposed remain comparatively less developer soluble. Photoresist compositions are described in Deforest, Photoresist Materials and Processes, McC

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Hill Book Company, New York, ch. 2, 1975 and by Moreau, Semiconductor Lithography, Principles, Practices and Materials, Plenum Press, New York, ch. 2.

More recently, chemically-amplified-type resists have been increasingly
5 employed, particularly for formation of sub-micron images and other high performance applications. Such photoresists may be negative-acting or positive-acting and generally include many crosslinking events (in the case of a negative-acting resist) or deprotection reactions (in the case of a positive-acting resist) per unit of photogenerated acid. In the case of positive chemically-amplified resists, certain cationic photoinitiators have
10 used to induce cleavage of certain "blocking" groups pendant from a photoresist binder or cleavage of certain groups that comprise a photoresist binder backbone. See, for example, U.S. Patents Nos. 5,075,199; 4,968,581; 4,883,740; 4,810,613; and 4,499,000 and Canadian Patent Application 2,001,384. Upon cleavage of the blocking group through exposure of a coating layer of such a resist, a polar functional group is formed
15 e.g., carboxyl or imide, which results in different solubility characteristics in exposed and unexposed areas of the resist coating layer. See also R.D. Allen et al., Proceedings SPIE, 2724:334-343 (1996); and P. Trefonas et al. Proceedings of the 11th International Conference on Photopolymers (Soc. Of Plastics Engineers), pp 44-58 (Oct. 6, 1995).

20 While currently available photoresists are suitable for many applications, photoresists also can exhibit significant shortcomings, particularly in high performance applications such as formation of highly resolved sub-half micron and sub-quarter micron features.

25 Consequently, interest has increased in photoresists that can be photoimaged with short wavelength radiation, including exposure radiation of about 250 nm or less, about 200 nm or less, such as wavelengths of about 248 nm (provided by KrF laser) or 193 nm (provided by an ArF exposure tool). See European Published Application EP915382A2. Use of such short exposure wavelengths can enable formation of sub-half micron features.
30 features. Accordingly, a photoresist that yields well-resolved images upon 248 nm exposure is desired.

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nm exposure could enable formation of extremely small (e.g. sub-0.25 μm) features to respond to constant industry demands for smaller dimension circuit patterns, e.g. to provide greater circuit density and enhanced device performance.

5 However, many current photoresists are generally designed for imaging at relatively higher wavelengths, such as G-line (436 nm) and I-line (365 nm) are generally unsuitable for imaging at short wavelengths such as sub-200nm. Even shorter wavelength resists, such as those effective at 248 nm exposures, also are generally unsuitable for sub-200 nm exposures, such as 193 nm imaging.

10

More specifically, current photoresists can be highly opaque to extremely short exposure wavelengths such as 193 nm, thereby resulting in poorly resolved images.

15

It thus would be desirable to have new photoresist compositions, particularly resist compositions that can be imaged at short wavelengths such as sub-200 nm or shorter wavelengths, particularly 193 nm.

SUMMARY OF THE INVENTION

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We have now found novel polymers and photoresist compositions that contain the polymers as a resin binder component. The photoresist compositions of the invention can provide highly resolved relief images upon exposure to extremely short wavelengths, particularly sub-200 nm wavelengths such as 193 nm.

25

Polymers of the invention contain a oxygen- and/or sulfur-containing heteroalicyclic ring that is preferably fused to the polymer backbone (i.e. at least one heteroalicyclic ring atoms as part of the polymer backbone). The heteroalicyclic ring contains one or more oxygen and/or sulfur atoms as ring members.

30

Preferred polymers of the invention also contain a carbon alicyclic group (i.e. a group that has all carbon ring members) that is fused to the polymer backbone, i.e. the

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alicyclic ring has at least two carbon ring members that comprise the polymer backbone. Preferred fused carbon alicyclic groups are provided by polymerization of cyclic (endocyclic double bond) compounds such as optionally substituted norbornene groups. We have found that incorporation of such carbon alicyclic groups into a polymer significantly increase plasma etch resistance of a photoresist containing the polymer.

Preferred heteroalicyclic polymer units may be substituted, e.g. by heteroalicyclic groups such as ethers (alkoxy) preferably having 1 to about 10 carbon atoms, alkyloxy preferably having 1 to about 10 carbon atoms, alkylsulfinyl preferably 1 to about 10 carbon atoms, alkylsulfonyl preferably having 1 to about 10 carbon atoms, and the like. It has been surprisingly found that such substituents can provide enhanced lithography results, particularly enhanced substrate adhesion.

For use in photoresist compositions, polymers of the invention also will contain one or more units that comprise photoacid-labile moieties. The photoacid-labile moiety may be a substituent of one or more of the above-mentioned units, such as a substituent of a polymerized vinyl alicyclic ether, vinyl alicyclic thioether or carbon alicyclic ether. The photoacid labile moiety also may be present as an additional polymer unit, e.g., a polymerized alkyl acrylate or alkylmethacrylate, particularly an acrylate having an alicyclic moiety such as methyladamantyl acrylate or methyladamantyl methacrylate. Preferred alicyclic photoacid-labile moieties are tertiary ester alicyclic hydrocarbon groups that have two or more fused or bridged rings. Preferred tertiary ester groups include optionally substituted adamantyl, particularly methyl adamantyl as mentioned above; optionally substituted fencyl groups, particularly ethyl fencyl; optionally substituted pinanyl; and optionally substituted tricyclo decanyl, particularly an alkyl substituted tricyclo decanyl such as 8-ethyl-8-tricyclodecanyl e.g. as provided by polymerization of 8-ethyl-8-tricyclodecanyl acrylate and 8-ethyl-8-tricyclodecanyl methacrylate. Additional alicyclic ester groups also will be suitable, including additional bicyclic, tricyclic and other polycyclic moieties.

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- 5 -

Polymers of the invention also may contain units in addition to the above. For example, polymers of the invention also may contain nitrile units such as provided by the polymerization of methacrylonitrile and acrylonitrile. Additional contrast enhancing groups also may be present in polymers of the invention, such as groups provided by the polymerization of methacrylic acid, acrylic acid, and such acids protected as photolabile esters, e.g. as provided by reaction of ethoxyethyl methacrylate, t-butoxy methacrylate, t-butylmethacrylate and the like.

Generally preferred polymers of the invention contain 3, 4 or 5 distinct repeating units, i.e. preferred are terpolymers, tetrapolymers and pentapolymers that contain more heteroalicyclic groups as disclosed herein.

Polymers of the invention are preferably employed in photoresists imaged with short wavelength radiation, and thus preferably will be substantially free of any phenyl or other aromatic groups. For example, preferred polymers contain less than about 5 mole percent aromatic groups, more preferably less than about 1 or 2 mole percent aromatic groups, more preferably less than about 0.1, 0.02, 0.04 and 0.08 mole percent aromatic groups and still more preferably less than about 0.01 mole percent aromatic groups. Particularly preferred polymers are completely free of aromatic groups. Aromatic groups can be highly absorbing of sub-200 nm radiation and thus are undesirable for polymers used in photoresists imaged with such short wavelength radiation.

The invention also provides methods for forming relief images, including methods for forming a highly resolved relief image such as a pattern of lines where each line has essentially vertical sidewalls and a line width of about 0.40 microns or less, even a width of about 0.25, 0.20 or 0.16 microns or less. The invention further provides articles of manufacture comprising substrates such as a microelectronic wafer substrate, liquid crystal display or other flat panel display substrate having coated thereon a polymer, photoresist or resist relief image of the invention. Other aspects of the invention are disclosed infra.

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DETAILED DESCRIPTION OF THE INVENTION

As discussed above, polymers of the invention contain a heteroalicyclic ring is preferably fused to a polymer backbone. The fused heterocyclic ring units contain 5 or more oxygen and/or sulfur atoms. By stating herein that a cyclic group is fused to a polymer backbone, it is meant that two ring members of the cyclic group, typically adjacent carbon atoms of the cyclic group, are also part of the polymer backbone. The fused ring can be provided by polymerizing a cyclic monomer that has an endocyclic double bond.

10 The oxygen and/or sulfur atoms of the heteroalicyclic ring are preferably ring members (bi-radical linkages), rather than e.g. a multiple bond group such as a thioketo ring member. Also, less preferred are groups that contain any such side groups such as a ketone or other carbonyl including ester, lactone, anhydride, etc.

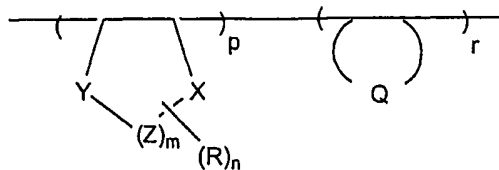
15 Preferred oxygen ring polymer units will be free of other hetero atoms such as sulfur (i.e. only oxygen and carbon ring members). Typically, the oxygen ring units contain a single oxygen ring atom and may have one or more ring substituents. As discussed above, it has been found that such ring substituents can significantly enhance 20 substrate adhesion.

Additionally, an oxygen heteroalicyclic group will be present in a polymer together with polymerized carbon alicyclic compounds such as optionally substituted norbornene. As referred to herein, the term "carbon alicyclic group" means each 25 member of the non-aromatic group is carbon. The carbon alicyclic group can have more endocyclic carbon-carbon double bonds, provided the ring is not aromatic.

Preferred polymers of the invention that contain oxygen heteroalicyclic units comprise a structure of the following Formula I:

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wherein X, Y, and each Z are each independently carbon or oxygen, with one of X, Y or Z being oxygen, and preferably no more than two of X, Y and Z being oxygen;

Q represents an optionally substituted carbon alicyclic ring fused to the polymer backbone (i.e. two Q ring members being adjacent carbons of the polymer backbone). The alicyclic ring suitably having from about 5 to about 18 carbon atoms and is suitably a single ring (e.g. cyclopentyl, cyclohexyl or cycloheptyl), or more preferably Q is polycyclic e.g. and contain 2, 3, 4 or more bridged, fused or otherwise linked ring systems. Preferred substituents of a substituted Q group include photoacid-labile moieties such as a photoacid-labile ester;

each R is the same or different non-hydrogen substituent such as cyano; optionally substituted alkyl preferably having 1 to about 10 carbon atoms; optionally substituted alkanoyl preferably having 1 to about 10 carbon atoms; optionally substituted alkoxy preferably having 1 to about 10 carbon atoms; optionally substituted alkylthio preferably having 1 to about 10 carbon atoms; optionally substituted alkylsulfinyl preferably having 1 to about 10 carbon atoms; optionally substituted alkylsulfonyl preferably having 1 to about 10 carbon atoms; optionally substituted carboxy preferably having 1 to about 10 carbon atoms (which includes groups such as -COOR' where R' is H or alkyl, including esters that are substantially non-reactive with photoacid); a photoacid-labile group such as a photoacid-labile ester e.g. a tert-butyl ester and the like; etc.

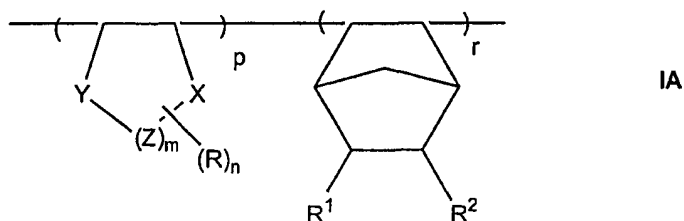
m is 1 (to provide a fused five-membered ring), 2 (to provide a fused six-membered ring), 3 (to provide a fused seven-membered ring), or 4 (to provide a fused eight-membered ring);

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n is an integer of from 0 (i.e. no R ring substituents), 1 (i.e. a single R ring substituent) to the maximum possible value permitted by the valences of the ring members, and preferably n is 0, 1, 2, 3, 4 or 5, and more preferably n is 0, 1, 2 or

p is the mole fraction of the fused oxygen ring units based on total units in polymer; and r is the mole fraction of the fused carbon alicyclic ring units based on units in the polymer, and p and r are each greater than zero.

As discussed above, preferred carbon alicyclic ring units are polymerized optionally substituted norbornene groups. Thus, preferred polymers that contain heteroalicyclic units comprise a structure of the following Formula IA:



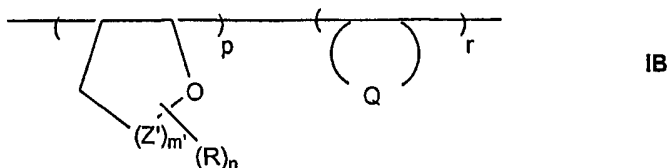
wherein X, Y, Z, R, m and n are the same specified for Formula I above;

R¹ and R² are each independently hydrogen or a non-hydrogen substituent halo (F, Cl, Br, I), nitro, cyano, optionally substituted alkyl (including cycloalkyl) preferably having from 1 to about 16 carbons; optionally substituted alkoxy preferably having from 1 to about 16 carbons; optionally substituted alkylthio preferably having from 1 to about 16 carbons; optionally substituted carboxy preferably have 1 to about 16 carbon atoms (which includes groups such as -COOR' where R' is H or C₁₋₈alkyl, including esters that are substantially non-reactive with photoacid); a lactone; an anhydride such as an itaconic anhydride group; a photoacid-labile group such as a photoacid-labile ester, particularly a photoacid-labile ester moiety with a tertiary ester group or a non-cyclic group such as t-butyl; and the like, or R¹ and R² may be taken together to form one or more rings fused to the depicted norbornyl ring;

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p is the mole fraction of the fused oxygen ring units based on total units in polymer; and r is the mole fraction of the fused optionally substituted norbornene units based on total units in the polymer, and p and r are each greater than zero.

- 5 Particularly preferred oxygen ring polymer units include those that have five ring members and an oxygen ring member adjacent to the polymer backbone. Accordingly, preferred are polymers that comprise a structure of the following Formula IB:



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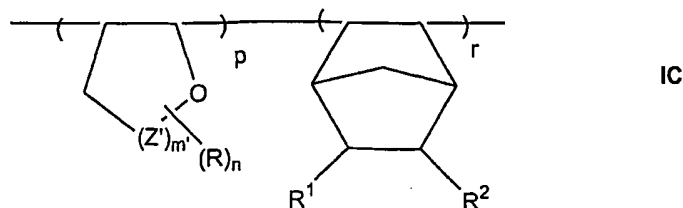
wherein each Z' is independently oxygen, sulfur or carbon, and preferably is carbon; m' is 1, 2, 3 or 4; and R and n are each the same as defined in Formula I and preferably n is 0, 1, 2, 3, 4 or 5, and more preferably n is 0, 1, 2 or 3;

Q is the same as defined in Formula I;

- 15 p is the mole fraction of the fused oxygen ring units based on total units in polymer; and r is the mole fraction of the fused carbon alicyclic ring units based on units in the polymer, and p and r are each greater than zero.

20

Preferred polymers of Formula IB contain polymerized norbornene units, and polymers that comprise a structure of the following Formula IC:

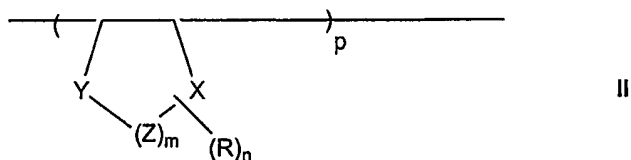


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wherein Z' , m' , R , n , and p are the same as defined in Formula IB; and R^1 , R^2 and r are the same as defined in Formula IA.

- 5 Preferred sulfur ring polymer units also will be free of other hetero atoms : oxygen (i.e. only sulfur and carbon ring members), or will contain only one or two hetero atoms such as oxygen, typically only one additional heteroatom such as ox

10 Preferred sulfur ring polymer units include those of the following Formula



wherein X , Y , and each Z are each independently carbon, oxygen or sulfur at least one of X , Y or Z being sulfur, and preferably no more than two of X , Y and being sulfur;

- 15 each R is the same or different non-hydrogen substituent such as cyano; optionally substituted alkyl preferably having 1 to about 10 carbon atoms; optionally substituted alkanoyl preferably having 1 to about 10 carbon atoms; optionally substituted alkoxy preferably having 1 to about 10 carbon atoms; optionally substituted alkylthio preferably having 1 to about 10 carbon atoms; optionally substituted alkylsulfinyl preferably 1 to about 10 carbon atoms; optionally substituted alkylsulfonyl preferably having 1 to about 10 carbon atoms; optionally substituted carboxy preferably having about 10 carbon atoms (which includes groups such as $-COOR'$ where R' is H or alkyl, including esters that are substantially non-reactive with photoacid); a photolabile group such as a photoacid-labile ester e.g. a tert-butyl ester and the like; etc.
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- 25 m is 1 (to provide a fused five-membered ring), 2 (to provide a fused six-membered ring), 3 (to provide a fused seven-membered ring) or 4 (to provide a fused eight-membered ring);

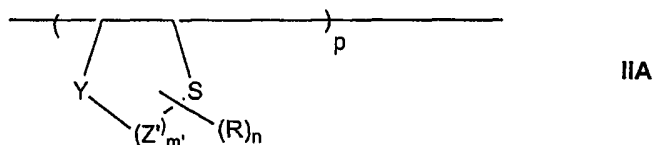
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n is an integer of 0 (no R substituents present), 1 (i.e. a single R ring substituent to the maximum possible substitution permitted by the valences of the ring member), preferably n is 0, 1, 2, 3, 4 or 5, and more preferably n is 0, 1, 2 or 3; and

p is greater than zero and is the mole fraction of the fused sulfur ring units on total units in the polymer.

Particularly sulfur ring polymer units include those that have five, six or seven ring members and an sulfur ring member adjacent to the polymer backbone, such as of the following Formula IIA:

10



wherein Y is the same as specified for Formula I above;

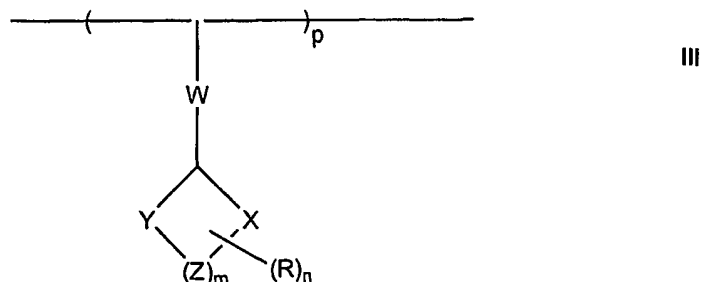
wherein each Z' is independently carbon, oxygen, or sulfur; and preferably is carbon; m' is 1, 2, 3 or 4; and R and n are each the same as defined in Formula I and preferably n is 0, 1, 2, 3, 4 or 5, and more preferably n is 0, 1, 2 or 3; and

p is greater than zero and is the mole fraction of the fused sulfur ring units on total units in the polymer.

Polymers of the invention also may contain oxygen or sulfur ring groups that are spaced from the polymer backbone. The spaced oxygen or sulfur ring group suitable for the invention contain a single ring, although polycyclic rings that contain one or more oxygen or sulfur ring members also will be suitable. Less preferred are groups where sulfur or oxygen is a bridgehead atom of a polycyclic group, particularly a bridgehead of a bicyclic group such as a oxonorbonyl or thionorbonyl group, especially if such oxonorbonyl or thionorbonyl group is present as part of an ester moiety.

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For example, suitable spaced oxygen and/or sulfur ring groups of polymer invention include those of the following Formula III:

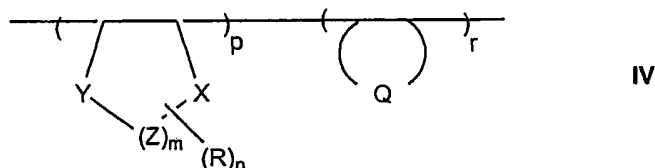


- 5 wherein W is a linker; X, Y, and each Z are each independently carbon, oxygen or sulfur, with at least one of X, Y or Z being oxygen or sulfur;
- each R is the same or different non-hydrogen substituent such as those non-hydrogen substituents specified for R in Formula I above;
- m is 1, 2, 3, 4 or 5; n is an integer of from 0 to the maximum value substituted
- 10 permitted by the valences of the ring members; and p is the mole percent of the unit in the polymer.

- Typical W linker groups of Formula III include e.g. optionally substituted alkylene particularly optionally substituted C₁₋₈ alkylene; optionally substituted
- 15 alkenylene particularly optionally substituted C₂₋₈ alkenylene; optionally substituted alkynylene particularly optionally substituted C₂₋₈ alkynylene; optionally substituted heteroalkylene particularly optionally substituted C₁₋₈ heteroalkylene; optionally substituted heteroalkenylene particularly optionally substituted C₂₋₈ heteroalkenylene; optionally substituted heteroalkynylene particularly optionally substituted C₂₋₈
- 20 heteroalkynylene; an ester linkage (i.e. -C(=O)O); and the like. In Formula III, the spaced oxygen or sulfur ring group may be a component of a photoacid-labile group such as a photoacid-labile ester group. Such groups may be provided by polymer of the corresponding acrylate or methacrylate groups.

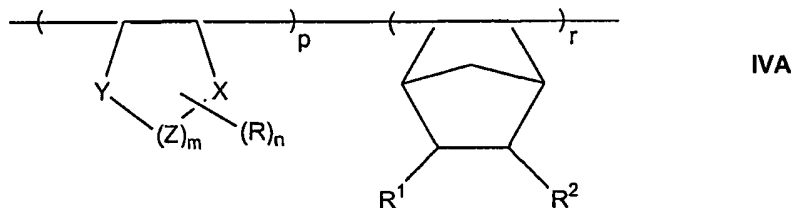
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Preferably, a sulfur heteroalicyclic group will be present in a polymer with polymerized carbon alicyclic olefin compounds. More specifically, preferred polymers of the invention include those that comprise a structure of the following Formula I:



wherein X, Y, Z, R, m, n and p are each the same as defined in Formula II
Q and r are the same as defined for Formula I above.

Preferred carbon alicyclic ring units are polymerized optionally substituted norbornene groups. Thus, preferred polymers that contain sulfur heteroalicyclic units comprise a structure of the following Formula IVA:



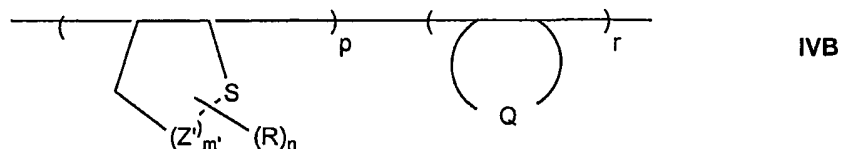
wherein X, Y, Z, R, m and n are the same specified for Formula II above;

R¹ and R² are the same as defined in Formula IA above;

p is the mole fraction of the fused sulfur ring units based on total units in the polymer; and r is the mole fraction of the fused optionally substituted norbornene units based on total units in the polymer, and p and r are each greater than zero.

Particularly preferred sulfur ring polymer units include those that have five, six, seven or eight ring members and a sulfur ring member adjacent to the polymer backbone.

Accordingly, preferred are polymers that comprise a structure of the following Formula IVB:

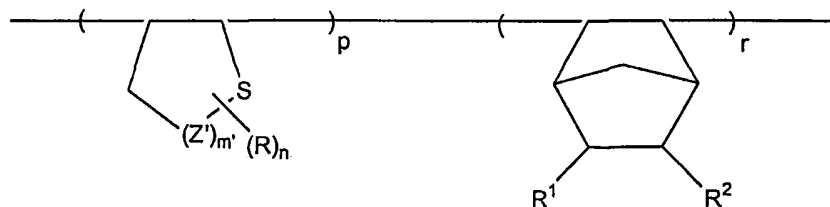


wherein each Z' is independently oxygen, sulfur or carbon, and preferably carbon; m' is 1, 2, 3 or 4; and R and n are each the same as defined in Formula I and preferably n is 0, 1, 2, 3, 4 or 5, and more preferably n is 1, 2 or 3;

Q is the same as defined in Formula I;

10 p is the mole fraction of the fused sulfur ring units based on total units in the polymer; and r is the mole fraction of the fused carbon alicyclic ring units based on total units in the polymer, and p and r are each greater than zero.

Preferred polymers of Formula IVB contain polymerized norbornene units. Preferred polymers that comprise a structure of the following Formula IVC:



wherein Z', m', R, n, and p are the same as defined in Formula IVB; and R¹, R² and r are the same as defined in Formula IA.

20

In the above Formulae I, IA, IB, IC, II, IIA, III, IV, IVA, IVB and IVC, as well as below Formulae V, VI and VII (together sometimes referred to herein simply as "formulae" or similar phrase), preferably R substituents of the depicted heteroalicyclic

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are electron-donating groups such as optionally substituted alkyl, optionally substituted alkoxy or optionally substituted alkylthio. Such electron-donating groups can facilitate polymerization of the corresponding vinyl heteroalicyclic monomer.

5 Preferred polymers of the invention will contain at least about 2 to 5 mole percent of fused heteroalicyclic units based on total units of the polymer; more preferably about 5 to 50 mole percent of fused heteroalicyclic units based on total units of the polymer; still more preferably from about 5 or 10 to about 40 or 50 percent of fused heteroalicyclic units based on total units of the polymer.

10

Preferred polymers of the invention will contain at least about 2 to 5 mole percent of carbon alicyclic units based on total units of the polymer; more preferably from about 5 to 50 mole percent of fused carbon alicyclic units based on total units of the polymer; still more preferably from about 5 or 10 to about 25 or 30 percent of fused carbon alicyclic units based on total units of the polymer.

15

In polymers of the invention that contain only heteroalicyclic units and carbon alicyclic units, preferably the heterocyclic units will be present in an amount of from about 5 to about 90 or 95 mole percent based on total polymer units, and the carbon alicyclic units will be present in an amount of from about 5 to about 90 or 95 mole percent based on total polymer units.

20

In polymers of the invention that consist of heteroalicyclic units, carbon alicyclic units and maleic anhydride units (i.e. heteroalicyclic:carbon alicyclic:maleic anhydride terpolymers), preferably the heterocyclic units will be present in an amount of from about 5 to about 10, 20, 30, 40, 50, 60, 70 or 80 mole percent based on total polymer units, the carbon alicyclic units (such as optionally substituted norbornene) will be present in an amount of from about 5 to about 10, 20, 30, 40, 50, 60, 70 or 80 mole percent based on total polymer units, and the maleic anhydride units will be present from about 5 to about 20, 30, 40 or 50 mole percent based on total polymer units; and more preferably from

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heterocyclic units will be present in an amount of from about 5 to about 10, 20, 30 or 50 or 60 mole percent based on total polymer units, the carbon alicyclic units will present in an amount of from about 5 to about 10, 20, 30, 40, 50 or 60 mole percent based on total polymer units, and the maleic anhydride units will be present from about 5 to about 10, 15, 20, 25, 30, 40, or 50 mole percent based on total polymer units. In some terpolymers, suitably either or both the heteroalicyclic or carbon alicyclic units will contain a photoacid labile substituents such as a photoacid-labile ester substituent

In the above the above formulae, the R, R¹ and R² substituents each can be a photoacid-labile groups. Photoacid-labile ester groups are generally preferred such as a tert-butyl ester, or an ester containing a tertiary alicyclic group. Such photoacid-labile esters may be directly pendant from a heteroalicyclic or carbon alicyclic polymer unit (i.e. -C(=O)OR, where R is tert-butyl or other non-cyclic alkyl group, or a tertiary alicyclic group), or the ester moieties may be spaced from the from a heteroalicyclic or carbon alicyclic polymer unit, e.g. by an optionally alkylene linkage (e.g. -(CH₂)₁₋₈C(=O)OR, where R is tert-butyl or other non-cyclic alkyl group, or a tertiary alicyclic group).

In any event, polymers of the invention preferably comprise contain one or more repeat units that comprise a photoacid-labile group. As discussed with respect to substituents R, R¹ and R² of the above formulae, the photoacid-labile may be a substituent of a heteroalicyclic or carbon alicyclic ring member. Alternatively, and generally preferred, the photoacid-labile moiety will be a polymer repeat unit distinct from repeat units containing a heteroalicyclic group.

Preferred photoacid-labile groups are ester groups, particularly esters that contain a tertiary alicyclic hydrocarbon ester moiety. Preferred tertiary alicyclic hydrocarbon ester moieties are polycyclic groups such as adamantyl, ethylfencyl or a tricyclo decyl moiety. References herein to a "tertiary alicyclic ester group" or other similar terms indicate that a tertiary alicyclic ring carbon is covalently linked to the ester oxygen.

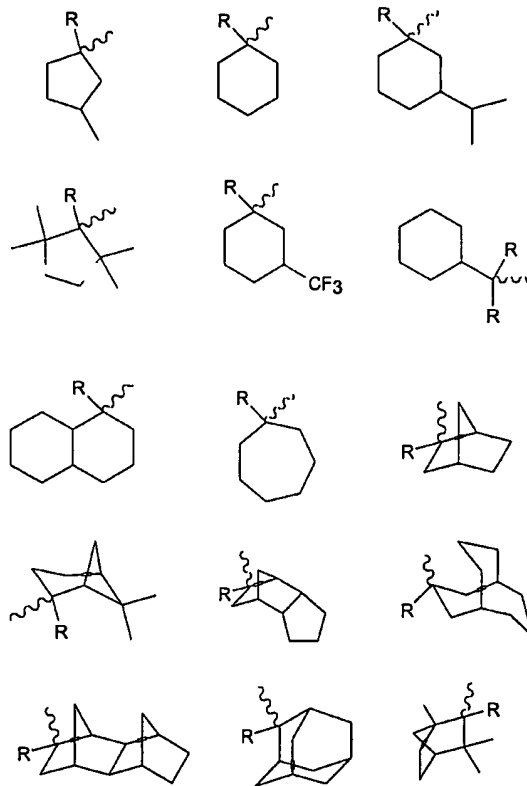
- 17 -

-C(=O)O-TR' where T is a tertiary ring carbon of alicyclic group R'. In at least a few cases, preferably a tertiary ring carbon of the alicyclic moiety will be covalently linked to the ester oxygen, such as exemplified by the below-depicted specifically preferred polymers. However, the tertiary carbon linked to the ester oxygen also can be exocyclic to the alicyclic ring, typically where the alicyclic ring is one of the substituents of an exocyclic tertiary carbon. Typically, the tertiary carbon linked to the ester oxygen is substituted by the alicyclic ring itself, and/or one, two or three alkyl groups having about 12 carbons, more typically 1 to about 8 carbons, even more typically 1, 2, 3 carbons. The alicyclic group also preferably will not contain aromatic substitution. Alicyclic groups may be suitably monocyclic, or polycyclic, particularly bicyclic or tricyclic groups.

Preferred alicyclic moieties (e.g. group TR' of -C(=O)O-TR') of photoacid labile ester groups of polymers of the invention have rather large volume. It has been found that such bulky alicyclic groups can provide enhanced resolution when used in copolymers of the invention.

More particularly, preferred alicyclic groups of photoacid labile ester groups have a molecular volume of at least about 125 or about 130 Å³, more preferably a molecular volume of at least about 135, 140, 150, 155, 160, 165, 170, 175, 180, 195, or 200 Å³. Alicyclic groups larger than about 220 or 250 Å³ may be less preferred in at least some applications. References herein to molecular volumes designate volumetric size as determined by standard computer modeling, which provides optimal chemical bond lengths and angles. A preferred computer program for determining molecular volume as referred to herein is Alchemy 2000, available from Tripos. For further discussion of computer-based determination of molecular size, see T. Omore, *Polymers for Advanced Technologies*, volume 4, pp. 277-287.

Particularly preferred tertiary alicyclic groups of photoacid-labile units include the following, where the wavy line depicts a bond to the carboxyl oxygen of the ester group, and R is suitably optionally substituted alkyl, particularly C₁₋₈ alkyl such as methyl, ethyl, etc.



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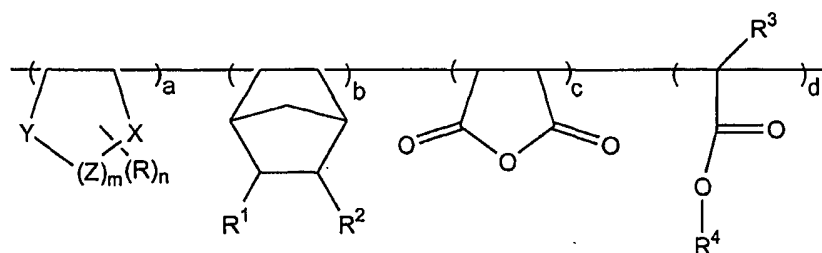
Polymers of the invention also may contain photoacid-labile groups that do not contain an alicyclic moiety. For example, polymers of the invention may contain photoacid-labile ester units, such as a photoacid-labile alkyl ester. Generally, the carboxyl oxygen (i.e. the carboxyl oxygen as underlined as follows: $-\text{C}(=\text{O})\underline{\text{O}}$) of a photoacid-labile ester will be covalently linked to the quaternary carbon. Branched photoacid-labile esters are generally preferred such as t-butyl and $-\text{C}(\text{CH}_3)_2\text{CH}(\text{C})$.

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Polymers of the invention also may contain additional units such as cyano lactone units or anhydride units. For example, acrylonitrile or methacrylonitrile may be polymerized to provide pendant cyano groups, or maleic anhydride may be polymerized to provide a fused anhydride unit.

5

Particularly preferred polymers of the invention include those that comprise the structure of the following Formula V:



10 wherein X, Y, Z, R, m and n are each the same as defined in Formula I above; R¹ and R² are each independently hydrogen or a non-hydrogen substituent specified for R¹ and R² in Formula IA above;

R³ is hydrogen or alkyl, particularly C₁₋₆ alkyl such as methyl;

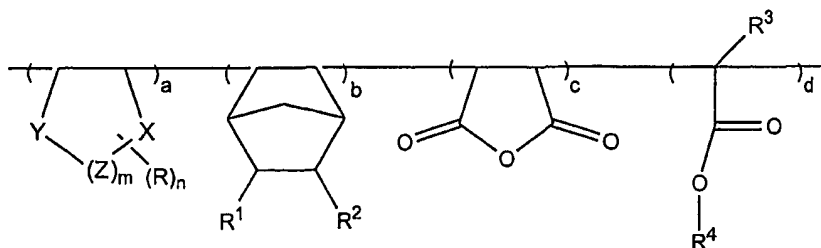
15 R⁴ is a group that renders the depicted ester photoacid-labile, such as a tertiary alicyclic group as discussed above, or a branched non-cyclic optionally substituted group, with the ester carboxyl group being directly bonded to a quaternary (i.e. no hydrogen substituents) carbon atom; and

a, b, c, and d are each greater than zero and are mole fractions of the respective polymer units.

20

Preferred polymers of the invention also include those of the following Formula VI:

- 20 -



wherein X, Y, Z, R, m and n are each the same as defined in Formula II at

R¹ and R² are each independently hydrogen or a non-hydrogen substituent

5 such as specified for R¹ and R² in Formula IA above;

R³ is hydrogen or alkyl, particularly hydrogen or C₁₋₆ alkyl such as methyl

R⁴ is a group that renders the depicted ester photoacid-labile, such as a tert
 alicyclic group as discussed above, or a branched non-cyclic optionally substituted

10 hydrogen substituents) carbon atom; and

a, b, c, and d are each greater than zero and are mole fractions of the respective
 polymer units.

In each of above Formulae V and VI, preferably "a" (mole fraction of
 15 heterocyclic units) is from about 2 to 50 mole percent based on total polymer unit;
 preferably "a" is from about 2 to about 40 mole percent based on total polymer unit;
 still more preferably "a" is from about 2 to about 30 mole percent based on total p
 units.

20 In each of above Formulae V and VI, preferably "b" (mole fraction of norbornane
 units) is from about 2 to 25 mole percent based on total polymer units; more preferably
 "b" is from about 2 to about 20 mole percent based on total polymer units; and still
 preferably "b" is from about 2 to about 15 or 20 mole percent based on total polymer
 units.

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In each of above Formulae V and VI, preferably "c" (mole fraction of anhydride units) is from about 0 (i.e. no anhydride units) to 50 mole percent based on total polymer units; more preferably "c" is from about 2 to about 40 mole percent based on total polymer units.

5

In each of above Formulae V and VI, preferably "d" (mole fraction of photolabile ester unit) is from about 2 to 70 mole percent based on total polymer units; preferably "d" is from about 5 or 10 to about 70 mole percent based on total polymer units; still more preferably "d" is from about 5 or 10 to about 50 mole percent based on total polymer units.

10

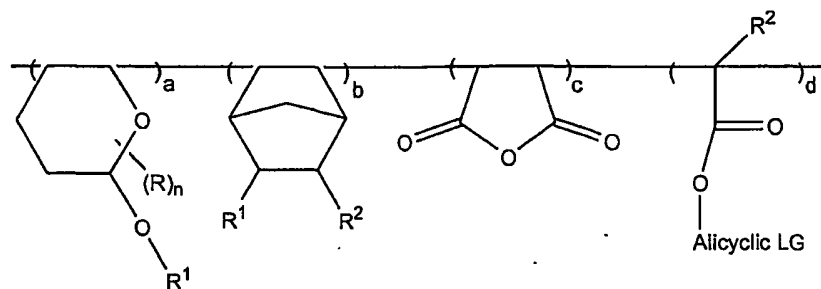
Preferred heteroalicyclic units of Formulae V and VI are the same as described above regarding Formulae IA and IIA respectively.

15

As discussed above, polymers of the invention are preferably employed in photoresists imaged at short wavelengths, particularly sub-200 nm such as 193 nm and 157 nm. Polymers also can be employed in photoresists imaged at higher wavelengths such as 248 nm. For such higher wavelength applications, the polymer may suitably contain aromatic units, e.g. polymerized styrene or hydrostyrene units.

20

Specifically preferred polymers of the invention include those of the following Formula VII:



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In Formula VII above, "Alicyclic LG" is the same as defined for alicyclic substituent R^4 in Formulae V and VI above and is preferably methyladamantyl, 8-8-tricyclodecanyl, ethylfencyl and the like; R^1 is C_{1-8} alkyl, preferably C_{1-4} alkyl, moiety that forms a photoacid-labile group; R^2 is suitably hydrogen or C_{1-8} alkyl as methyl, ethyl, propyl and the like; $R^{1'}$ and $R^{2'}$ are the same as defined for R^1 and R^2 respectively in Formula IA above; and a, b, c and d are mole percents of the specified units in the polymer based on total polymer units. Preferably a (mole percent of optional alicyclic units) is from 1 to about 5, 10, 20, 30, 40, 50 or 60 mole percent; b (mole percent of optionally substituted norbornene units) is from 1 to about 5, 10, 20, 30 or 60 mole percent; c (mole percent of maleic anhydride units) is from 1 to about 20, 30, 40, or 50 mole percent. Units d (acrylate photoacid-labile units) may be not present (i.e. d is zero) where the heterocyclic or norbornene units contain a photoacid-labile units, or d may be suitably present at from about 2 to 10, 20, 30, 40 or 50 mole percent based on total polymer units.

As discussed, various moieties may be optionally substituted, including groups in Formulae I, IA, II, IIA, III, IV, IVA, IVB, IVC, V, VI, and VII. A "substituted" substituent may be substituted at one or more available positions, typically 1, 2, or 3 positions by one or more suitable groups such as e.g. halogen (particularly F, Cl or Br); cyano; C_{1-8} alkyl; C_{1-8} alkoxy; C_{1-8} alkylthio; C_{1-8} alkylsulfonyl; C_{2-8} alkenyl; C_{2-8} alkynyl; hydroxyl; nitro; alkanoyl such as a C_{1-6} alkanoyl e.g. acyl and the like; and the like.

Preferred alkanoyl groups, including as specified in the above formulae, with one or more keto groups, such as groups of the formula $-C(=O)R''$ where R'' is hydrogen or C_{1-8} alkyl. Suitable lactone groups, including as specified in the above formulae, include alpha-butyrolactone groups and the like.

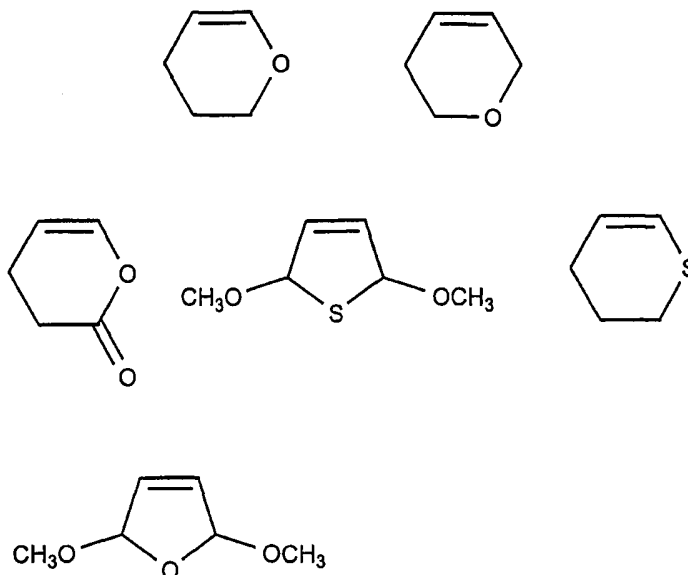
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Polymers of the invention can be prepared by a variety of methods. One method is an addition reaction which may include free radical polymerization, e.g. reaction of selected monomers to provide the various units as discussed above in the presence of a radical initiator under an inert atmosphere (e.g., N₂ or argon) and at elevated temperatures such as about 70°C or greater, although reaction temperatures vary depending on the reactivity of the particular reagents employed and the boiling of the reaction solvent (if a solvent is employed). Suitable reaction solvents include tetrahydrofuran, ethyl lactate and the like. Suitable reaction temperatures for any particular system can be readily determined empirically by those skilled in the art on the present disclosure. A variety of free radical initiators may be employed. For example, azo compounds may be employed such as azo-bis-2,4-dimethylpentanen Peroxides, peresters, peracids and persulfates also could be employed.

Other monomers that can be reacted to provide a polymer of the invention identified by those skilled in the art. For example, to provide photoacid-labile units suitable monomers include e.g. methacrylate or acrylate that contains the appropriate group substitution (e.g. tertiary alicyclic, t-butyl, etc.) on the carboxy oxygen of the group. Maleic anhydride is a preferred reagent to provide fused anhydride polymer units. Itaconic anhydride also is a preferred reagent to provide anhydride polymer units, preferably where the itaconic anhydride has been purified such as by extraction with chloroform prior to polymerization. Vinyl lactones are also preferred reagents, such as alpha-butyrolactone.

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Some suitable vinyl (endocyclic double bond) heterocyclic monomers that polymerized to provide polymers of the invention include the following:



Preferably a polymer of the invention will have a weight average molecular weight (M_w) of about 800 or 1,000 to about 100,000, more preferably about 2,000 to about 30,000, still more preferably from about 2,000 to 15,000 or 20,000, with a molecular weight distribution (M_w/M_n) of about 3 or less, more preferably a molecular weight distribution of about 2 or less. Molecular weights (either M_w or M_n) of the polymers of the invention are suitably determined by gel permeation chromatography.

10

Polymers of the invention used in photoresist formulations should contain sufficient amount of photogenerated acid labile ester groups to enable formation of relief images as desired. For instance, suitable amount of such acid labile ester groups will be at least 1 mole percent of total units of the polymer, more preferably about 15 mole percent, still more typically about 3 to 30 or 40 mole percent of total polymer. See the examples which follow for exemplary preferred polymers.

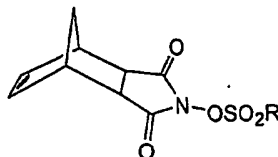
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As discussed above, the polymers of the invention are highly useful as a resin binder component in photoresist compositions, particularly chemically-amplified photoresists. Photoresists of the invention in general comprise a photoactive component and a resin binder component that comprises a polymer as described above.

5

The resin binder component should be used in an amount sufficient to render a coating layer of the resist developable with an aqueous alkaline developer.

The resist compositions of the invention also comprise a photoacid generator ("PAG") that is suitably employed in an amount sufficient to generate a latent image in a coating layer of the resist upon exposure to activating radiation. Preferred PAGs for 193 nm and 248 nm imaging include imidosulfonates such as compounds of the following formula:

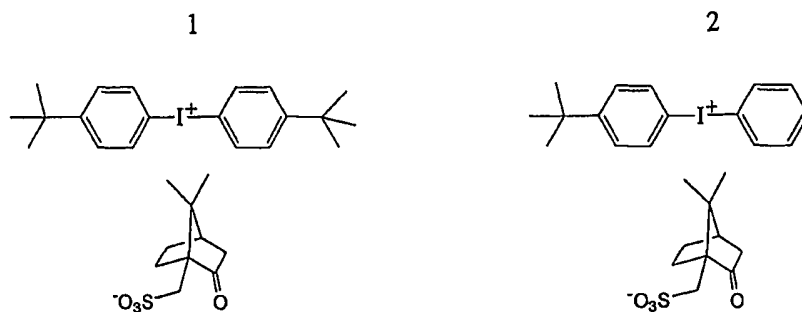


15 wherein R is camphor, adamantane, alkyl (e.g. C₁₋₁₂ alkyl) and perfluoroalkyl such as perfluoro(C₁₋₁₂alkyl), particularly perfluorooctanesulfonate, perfluorononanesulfonate and the like. A specifically preferred PAG is N-[(perfluorooctanesulfonyl)oxy]-5-norbornene-2,3-dicarboximide.

20 Sulfonate compounds are also suitable PAGs, particularly sulfonate salts. Suitable agents for 193 nm and 248 nm imaging are the following PAGS 1 and 2

25

30



Such sulfonate compounds can be prepared as disclosed in European Patent Application 9611811.2 (publication number 0783136), which details the syntheses above PAG 1.

Also suitable are the above two iodonium compounds complexed with an
10 other than the above-depicted camphorsulfonate groups. In particular, preferred are
include those of the formula RSO_3^- where R is adamantane, alkyl (e.g. C_{1-12} alkyl),
perfluoroalkyl such as perfluoro (C_{1-12} alkyl), particularly perfluorooctanesulfonate,
perfluorobutanesulfonate and the like.

15 Other known PAGS also may be employed in the resists of the invention. Particularly for 193 nm imaging, generally preferred are PAGS that do not contain aromatic groups, such as the above-mentioned imidosulfonates, in order to provide enhanced transparency.

20 A preferred optional additive of resists of the invention is an added base, particularly tetrabutylammonium hydroxide (TBAH), or tetrabutylammonium lac which can enhance resolution of a developed resist relief image. For resists imag 193 nm, a preferred added base is a hindered amine such as diazabicyclo undecen diazabicyclononene. The added base is suitably used in relatively small amounts, 25 about 0.03 to 5 percent by weight relative to the total solids.

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Photoresists of the invention also may contain other optional materials. For example, other optional additives include anti-striation agents, plasticizers, speed enhancers, etc. Such optional additives typically will be present in minor concentration in a photoresist composition except for fillers and dyes which may be present in relatively large concentrations, e.g., in amounts of from about 5 to 30 percent by weight of the total weight of a resist's dry components.

The resists of the invention can be readily prepared by those skilled in the art. For example, a photoresist composition of the invention can be prepared by dissolving components of the photoresist in a suitable solvent such as, for example, ethyl lactate, ethylene glycol monomethyl ether, ethylene glycol monomethyl ether acetate, propylene glycol monomethyl ether; propylene glycol monomethyl ether acetate and 3-ethoxypropionate. Typically, the solids content of the composition varies between about 35 percent by weight of the total weight of the photoresist composition. The resist and photoactive components should be present in amounts sufficient to provide a coating layer and formation of good quality latent and relief images. See the examples which follow for exemplary preferred amounts of resist components.

The compositions of the invention are used in accordance with generally known procedures. The liquid coating compositions of the invention are applied to a substrate such as by spinning, dipping, roller coating or other conventional coating techniques. When spin coating, the solids content of the coating solution can be adjusted to provide a desired film thickness based upon the specific spinning equipment utilized, the viscosity of the solution, the speed of the spinner and the amount of time allowed for spinning.

The resist compositions of the invention are suitably applied to substrates conventionally used in processes involving coating with photoresists. For example, the composition may be applied over silicon wafers or silicon wafers coated with silicon dioxide for the production of microprocessors and other integrated circuit components.

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Aluminum-aluminum oxide, gallium arsenide, ceramic, quartz, copper, glass substrate and the like are also suitably employed.

Following coating of the photoresist onto a surface, it is dried by heating to remove the solvent until preferably the photoresist coating is tack free. Thereafter, the coating is imaged through a mask in conventional manner. The exposure is sufficient to effectively activate the photoactive component of the photoresist system to produce a pattern image in the resist coating layer and, more specifically, the exposure energy typically ranges from about 1 to 100 mJ/cm², dependent upon the exposure tool and the components of the photoresist composition.

As discussed above, coating layers of the resist compositions of the invention are preferably photoactivated by a short exposure wavelength, particularly a sub-300 nm exposure wavelength. As discussed above, 193 nm is a particularly preferred exposure wavelength. 157 nm also is a preferred exposure wavelength. However, other resist compositions of the invention also may be suitably imaged at higher wavelengths. For example, a resin of the invention can be formulated with an appropriate PAG sensitizer if needed and imaged at higher wavelengths e.g. 248 nm or 365 nm.

Following exposure, the film layer of the composition is preferably baked at temperatures ranging from about 70°C to about 160°C. Thereafter, the film is developed. The exposed resist film is rendered positive working by employing a polar developer, preferably an aqueous-based developer such as quaternary ammonium hydroxide solutions such as a tetra-alkyl ammonium hydroxide solution; various amine solutions, preferably a 0.26 N tetramethylammonium hydroxide, such as ethyl amine, n-propyl amine, diethyl amine, di-n-propyl amine, triethyl amine, or methyldiethyl amine; cyclic amines such as diethanol amine or triethanol amine; cyclic amines such as pyrrolidine, pyridine, etc. In general, development is in accordance with procedures recognized in the art.

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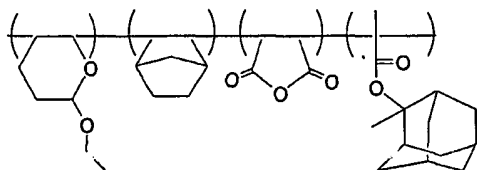
- 29 -

Following development of the photoresist coating over the substrate, the developed substrate may be selectively processed on those areas bared of resist, for example by chemically etching or plating substrate areas bared of resist in accordance with procedures known in the art. For the manufacture of microelectronic substrates, e.g., the manufacture of silicon dioxide wafers, suitable etchants include a gas etchant, e.g. a halogen plasma etchant such as a chlorine or fluorine-based etchant such as a CF_4/CHF_3 etchant applied as a plasma stream. After such processing, resist may be removed from the processed substrate using known stripping procedures.

10 All documents mentioned herein are incorporated herein by reference. The following non-limiting examples are illustrative of the invention.

Examples 1-2: Polymer syntheses

Example 1: Synthesis of tetrapolymer of: 2-(6-ethoxy)tetrahydropyran: norbornene: maleic anhydride: 2-methyladamantyl (respective molar ratio of units of 10:20:30:40)



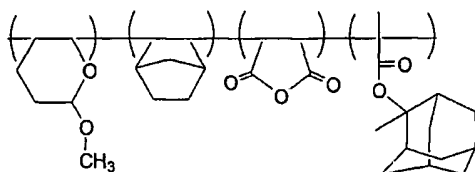
Composition 10/20/30/40

A mixture of 2-methyladamantyl methacrylate (60.0 g), maleic anhydride (12.03 g), norbornene (12.03 g), 3,4-dihydro-2-ethoxy-2-H-pyran (8.20 g) and V601 (photoinitiator; 3.73 g; 5 mole % of total monomers) in 99.07 g (1/1=monomer/solvent) of anhydride inhibitor free tetrahydrofuran was placed in a round-bottomed flask. stirring for 5 minutes (until all solids were dissolved in the solvent), the flask was a pre-heated 70°C oil bath. The reaction mixture was stirred at that temperature for 25 hours. After cooling, 99.07 g of THF was added to the reaction mixture. The polymer was isolated by precipitation into 2.0 L of hexane/isopropyl alcohol (1:1 wt.%). The suspension was stirred for 120 minutes. Then, the polymer was filtered off, and the

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filtered polymer was washed with an additional 200 mL of hexane. The polymer dried in a vacuum oven at 40°C for overnight (about 16 hours). Yield = 76.3%.

Example 2: Synthesis of tetrapolymer of: 2-(6-methoxy)tetrahydropyran
norbornene: maleic anhydride: 2-methyladmantyl (respective molar ratio of units of
10:20:30:40)



Composition 10/20/30/40

The title polymer was prepared by the same general procedures as disclosed above in Example 1, except 7.31 g of 3,4-dihydro-2-methoxy-2-H-pyran was used in place of 3,4-dihydro-2-ethoxy-2-H-pyran. Yield of polymer was 78.4 %.

Examples 3-6: Syntheses of monomers useful in preparation of polymers of the invention.

Example 3: EtTCD Methacrylate monomer synthesis

8-ethyl-8-tricyclodecanylmethacrylate (EtTCD methacrylate) was prepared following using the reagents and amounts thereof as specified in the following table.

Material	Amt (g)	Amt (ml)	Moles	Source
TCD	150.22		1.00	TCD
Ethylmagnesiumchloride(25%)	390.85	~379.5	~1.10	ACR
Methacryloyl chloride	120.22	~112.4	~1.15	Aldrich
Tetrahydrofuran	480	540		Aldrich

All reaction glassware was dried in the oven overnight at 100°C. The glassware was set up and cooled under a stream of nitrogen. The reaction was carried out under a blanket of nitrogen.

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To a 2L 3N-RB flask fitted with a gas inlet, thermometer, overhead stirrer rubber septum was added 400g of ethylmagnesium chloride, 25 wt% solution in tetrahydrofuran (clear, amber solution) via a double tipped needle using nitrogen pressure. The mixture was cooled to -25 to -30°C using a dry ice/isopropanol bath. The ethylmagnesium chloride solution was cooling the 153.6g of tricyclodecane (TCD) was dissolved in 480g of tetrahydrofuran. To a 1L 3N-RB flask equipped with a glass stopper and a rubber septum was added the 153.6g of TCD. The anhydrous, inhibitor free tetrahydrofuran was transferred to the 1L flask via a double tipped needle using nitrogen pressure. When the ethylmagnesium chloride was at -25 to -30°C, TCD/THF solution was transferred over a 2hr period to the 2L 3N-RB flask containing the ethylmagnesium chloride via a double tipped needle using nitrogen pressure. The cooling bath was removed and the reaction mixture was stirred for 2 hr. After stirring 2 hr the mixture was again cooled to -25 to -30°C using a dry ice/isopropanol bath. Methacryloyl chloride (120.22g) was then added dropwise over a 1 hour period using a 125ml pressure equalizing dropping funnel. The reaction was allowed to come to room temperature with overnight stirring. A white precipitate developed from the clear colored reaction solution. Water (DI) was added until all of the salts had dissolved (~500ml) and two distinct layers were seen. The layers were separated and the organic (upper) layer was washed with 2x400ml DI water then dried over magnesium sulfate. The THF was removed leaving 258g of an orange oil. The orange oil was dissolved in hexane then passed through a 400g silica gel plug which had been pre-conditioned with hexane. The silica was washed with hexane until all of the product was removed (collected in filtrate on a TLC plate and illuminate under short UV). The hexane was removed leaving 202.8g of an clear, colorless oil. Theoretical yield: 248.4g; yield: 81.6%

Example 4: Synthesis of Norbornene Valerolactone

A solution of valerolactone (50.1 g) in 150 mL of anhydrous THF was placed in a three-neck-bottomed flask at -78°C (Dry Ice/acetone). To it, solution of LDA (2.0 M) in 250 mL anhydrous THF was added dropwise. The reaction mixture was stirred

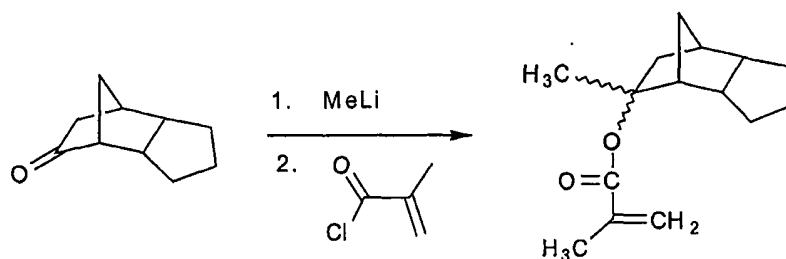
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this temperature for 4 hours. Then, the thermal cracking of paraformaldehyde (36 excess) was bubbled into the reaction mixture. After the paraformaldehyde was cracked, the reaction mixture was stirred at the same bath and stirred for overnight. Then, the solvent was removed by rotary pump and the residue was added 500 ml
 5 CH_2Cl_2 and washed with NaHCO_3 (aq, sat.) and water several times (3 x 500mL combination organic solvent was dried over MgSO_4 and the solvent was removed by rotary pump. The desired product was distilled under vacuum (135-140°C/8mmHg).

The methylene-valerolactone was dissolved in dichloromethane and freshly cracked cyclopentadiene was added. The reaction mixture was stirred at room
 10 temperature for 3 hours, then heated to 40°C, and held at 40°C overnight. The reaction mixture was then slowly cooled to room temperature. The methylene chloride was removed under reduced pressure, leaving an oil. The crude oil was then distilled under reduced pressure to afford pure product.

15

Example 5: Synthesis of 8-methyltricyclodecanyl methacrylate:

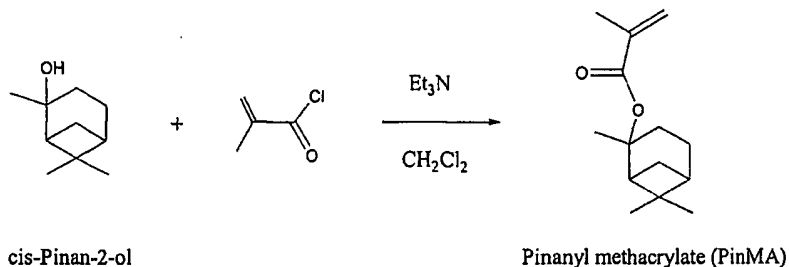


A solution of 125 ml of 1.4 M methyl lithium (in ethyl ether) in 100 ml of
 20 was decanted into a three neck round-bottom flask at an ice-water bath. To it, a solution of 24.00 g of tricyclo[5.2.1.0]decan-8-one in hexane was added dropwise. After the reaction mixture was stirred for 4 hours at 0°C. Then, a solution of 16 ml of methacryloyl chloride in 100 ml of hexane was added dropwise at 0°C. After addition, the reaction mixture was stirred at the same bath for overnight (16 hours). After filtration of
 25 white salts, the organic layer was washed with water three times (3 x 300 ml). The

washed organic layer was dried over anhydrous MgSO_4 . The organic solvent was removed by a rotary pump to give the crude title monomer (23.5 g). The monomer was purified by a flash column chromatography (purity >98%, silica gel with hexane). NMR: 6.05 (1H), 5.50 (1H), 1.95 (3H), 1.65 (3H), 2.25-0.85 (14H).

5

Example 6: Synthesis of pinanyl methacrylate



10 **Materials used:**

	Amount Charged	Moles	Source
cis-Pinan-2-ol	15.43 g	0.10	Fluka
Et ₃ N	12.14 g	0.12	Aldrich, distilled
Methacryloyl chloride	13.07 g	0.125	Aldrich, distilled
CH ₂ Cl ₂	230 mL		Aldrich, distilled

Procedure:

15 All reaction glassware and needles were dried and flushed with dry N₂ before use and the reaction was carried out under nitrogen atmosphere.

1) Into a 500 mL 3-neck round-bottom-flask equipped with an addition funnel and magnetic stirrer were added 15.43 g of cis-pinane-2-ol and 200 mL of dry CH_2Cl_2 (Stirred over CaH_2 overnight, then distilled and stored over activated molecular sieves). The resulting colorless solution was cooled with an ice-water bath.

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- 2) Triethylamine (12.14 g) was added through the addition funnel to the cooled (solution over 10 min. After added, the resulting solution was kept in a dry-ice bath (-67 °C).
- 3) A CH₂Cl₂ (30 mL) solution of methacryloyl chloride (13.07 g) was added drop over 20 min. The resulting orangish suspension was allowed to warm to room temperature and stirred for 2 h.
- 4) The chloride salts were filtered off. The filtrate was washed with saturated Na solution (2 x 200 mL), then DI water (3 x 200 mL) , and dried over anhydrous MgSO₄.
- 5) The slightly yellow CH₂Cl₂ solution was concentrated on a rotary evaporator temperature kept below 35°) to yield a clear slightly yellow liquid product. Yield 79%. The product was judged pure by NMR.

Example 7: Photoresist preparation and lithographic processing

- A photoresist of the invention is prepared by mixing the following components with amount expressed as weight percents based on total weight of the resist composition:

<u>Resist components</u>	<u>Amount (wt. % based on total)</u>
Resin binder	28.2
20 Photoacid generator	0.52
Basic additive	0.03
Surfactant	0.03

- The resin binder is the polymer of Example 2 above. The photoacid generator is triphenylsulfonium triflate. The basic additive is triisopropylamine. The surfactant is Silwet (Dow Chemical). Those resist components were formulated at 16 wt. % in a solvent of 2-heptanone.

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The formulated resist composition is spin coated onto HMDS vapor prime silicon wafers and softbaked via a vacuum hotplate at 130°C for 60 seconds. The coating layer is exposed through a photomask at 193 nm using an ISI microstepper then the exposed coating layers are post-exposure baked (PEB) at about 130°C. The coated wafers are then treated with 0.26N aqueous tetramethylammonium hydroxide solution to develop the imaged resist layer and provide a relief image.

Highly resolved 0.13 μm equal lines and spaces (1:1) were obtained.

10 Example 8: Comparative example

A resist formulation was prepared of essentially the same components and amounts thereof as in Example 7 above, but where the polymer (resin binder) did contain a polymerized ether, or other heteroalicyclic unit. The resist was processed as described in Example 7. The smallest resolved equal lines and spaces (1:1) that could be obtained were 0.14 μm .

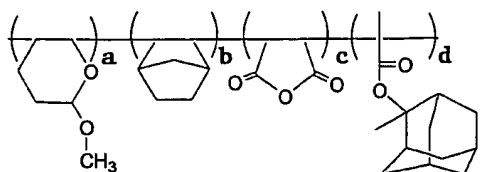
Example 9: Plasma etch tests

Oxide plasma etch rates of polymers of the invention were examined.

20 A first (comparative) terpolymer was tested for etch rates. That terpolymer contained polymerized units of p-hydroxystyrene, styrene and t-butylacrylate in respective molar ratios of 65:20:15.

25 Three tetrapolymers of the invention (referred to below as Polymers 1, 2 and 3 respectively) having the following structure were then tested for etch rates.

- 36 -



In Polymer 1, the molar ratio of polymer units a:b:c:d was 10:20:30:40.

In Polymer 2, the molar ratio of polymer units a:b:c:d was 10:15:25:50.

5 In Polymer 3, the molar ratio of polymer units a:b:c:d was 10:10:20:60.

Polymer 1 exhibited three percent greater oxide etch rate resistance than the comparative hydroxystyrene/styrene/t-butylacrylate terpolymer. Polymer 2 exhibited
 10 percent greater oxide etch rate resistance than the comparative hydroxystyrene/styrene/t-butylacrylate terpolymer. Polymer 3 exhibited eight percent greater etch rate resistance than the comparative hydroxystyrene/styrene/t-butylacrylate terpolymer.

The foregoing description of the invention is merely illustrative thereof, and it is understood that variations and modification can be made without departing from the
 15 or scope of the invention as set forth in the following claims.

What is claimed is:

1. A photoresist composition comprising a photoactive component and a polymer that comprises: i) a heteroalicyclic group fused to the polymer backbone contains one or more oxygen or sulfur ring members; ii) a carbon alicyclic group fused to the polymer backbone; and iii) a photoacid-labile moiety.
2. The photoresist of claim 1 wherein the heteroalicyclic group has an oxygen ring member.
3. The photoresist of claim 1 wherein the heteroalicyclic group has a sulfur ring member.
4. The photoresist of any one of claims 1 through 3 wherein the carbon alicyclic group is a polymerized norbornene group.
5. The photoresist of any one of claims 1 through 4 wherein the heteroalicyclic group has a non-hydrogen ring substituent.
6. The photoresist of any one of claims 1 through 5 wherein the photoacid-labile moiety is a substituent of the heteroalicyclic group and/or the carbon alicyclic group.
7. The photoresist of any one of claims 1 through 6 wherein the photoacid-labile moiety is a polymer unit separate from the heteroalicyclic group or the carbon alicyclic group.
8. The photoresist of claim 7 wherein the polymer comprises a polymerizable acrylate that comprises a photoacid-labile moiety.
9. The photoresist of any one of claims 1 through 8 wherein the polymer further comprises lactone and/or anhydride units.

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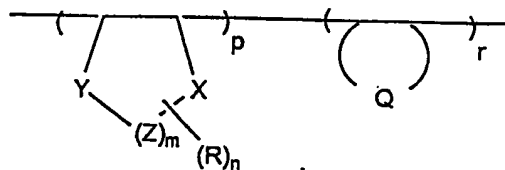
10. The photoresist of any one of claims 1 through 9 wherein the polymer further comprises maleic anhydride units.

11. The photoresist of any one of claims 1 through 10 wherein the heteroalicyclic group fused to the polymer backbone does not contain an unsaturated oxygen.

12. The photoresist of any one of claims 1 through 11 wherein the heteroalicyclic group fused to the polymer backbone does not contain an unsaturated sulfur.

13. The photoresist of any one of claims 1 through 11 wherein the heteroalicyclic group fused to the polymer backbone is not an anhydride or lactone.

14. The photoresist of claim 1 wherein the polymer comprises a structure of the following Formula I:



wherein X, Y, and each Z are each independently carbon or oxygen, with one of X, Y or Z being oxygen;

Q represents an optionally substituted carbon alicyclic ring with two ring members being adjacent carbons of the polymer backbone;

each R is the same or different non-hydrogen substituent;

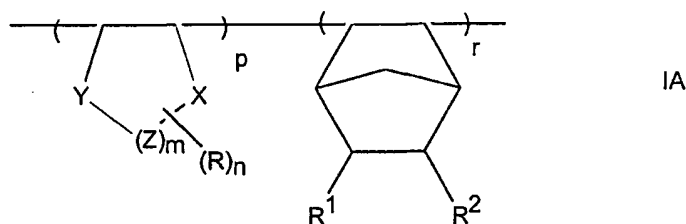
m is 1, 2, 3 or 4;

- 39 -

n is an integer of from 0 to the maximum value permitted by the valences of ring members;

p is the mole fraction of the fused oxygen ring units based on total units in polymer; and r is the mole fraction of the fused carbon alicyclic ring units based on units in the polymer, and p and r are each greater than zero.

15. The photoresist of claim 1 wherein the polymer comprises a structure of the following Formula IA:



wherein X, Y, and each Z are each independently carbon or oxygen, with at least one of X, Y or Z being oxygen;

each R is the same or different non-hydrogen substituent;

m is 1, 2, 3 or 4;

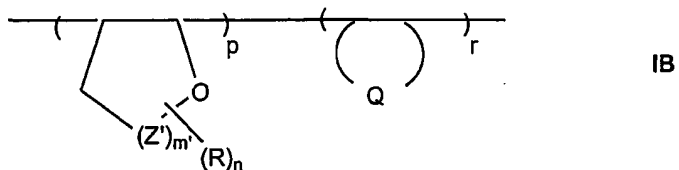
n is an integer of from 0 to the maximum value permitted by the valences of ring members;

R¹ and R² are each independently hydrogen or a non-hydrogen substituent

p is the mole fraction of the fused oxygen ring units based on total units in polymer; and r is the mole fraction of the fused optionally substituted norbornene units based on total units in the polymer, and p and r are each greater than zero.

- 40 -

16. The photoresist of claim 1 wherein the polymer comprises a structure of the following Formula IB:



wherein Z' is oxygen, sulfur or carbon; m' is 1, 2, 3 or 4;

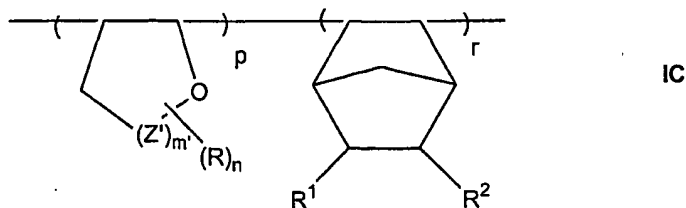
Q represents an optionally substituted carbon alicyclic ring with two ring members being adjacent carbons of the polymer backbone;

each R is the same or different non-hydrogen substituent;

n is an integer of from 0 to the maximum value permitted by the valences of the ring members;

p is the mole fraction of the fused oxygen ring units based on total units in the polymer; and r is the mole fraction of the fused carbon alicyclic ring units based on units in the polymer, and p and r are each greater than zero.

17. The photoresist of claim 1 wherein the polymer comprises a structure of the following Formula IC:



wherein Z' is oxygen, sulfur or carbon; m' is 1, 2, 3 or 4;

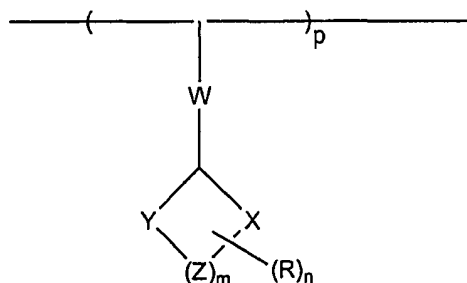
each R is the same or different non-hydrogen substituent;

n is an integer of from 0 to the maximum value substitution permitted by the valences of the ring members;

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R^1 and R^2 are each independently hydrogen or a non-hydrogen substituent;
 p is the mole fraction of the fused oxygen ring units based on total units in the polymer; and r is the mole fraction of the fused carbon alicyclic ring units based on units in the polymer, and p and r are each greater than zero.

18. The photoresist of claim 1 wherein the polymer comprises units of the following Formula III:



III

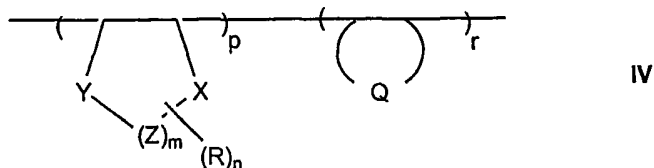
wherein W is a linker;

wherein X , Y , and each Z are each independently carbon, oxygen, or sulfur; at least one of X , Y or Z being oxygen or sulfur;

each R is the same or different non-hydrogen substituent;

m is 1, 2, 3, 4 or 5; n is an integer of from 0 to the maximum value substituted by the valences of the ring members; and p is the mole percent of the units of the polymer.

19. The photoresist of claim 1 wherein the polymer comprises a structure the following Formula IV:



wherein X, Y, and each Z are each independently carbon or sulfur, with at least one of X, Y or Z being sulfur;

Q represents an optionally substituted carbon alicyclic ring with two ring members being adjacent carbons of the polymer backbone;

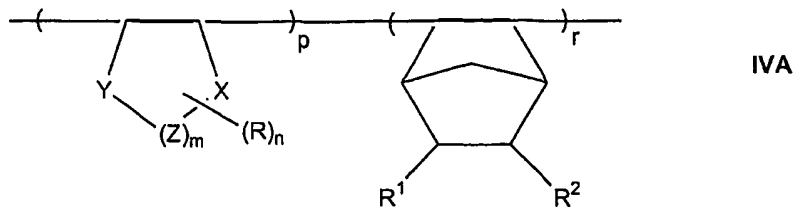
each R is the same or different non-hydrogen substituent;

m is 1, 2 or 3;

n is an integer of from 0 to the maximum value permitted by the valences of the ring members;

p is the mole fraction of the fused oxygen ring units based on total units in the polymer; and r is the mole fraction of the fused carbon alicyclic ring units based on units in the polymer, and p and r are each greater than zero.

20. The photoresist of claim 1 wherein the polymer comprises a structure the following Formula IVA:



wherein X, Y, and each Z are each independently carbon, oxygen, or sulfur, with at least one of X, Y or Z being sulfur;

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each R is the same or different non-hydrogen substituent;

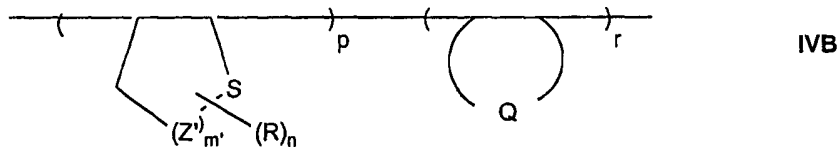
m is 1, 2 or 3;

n is an integer of from 0 to the maximum value permitted by the valences ring members;

R^1 and R^2 are each independently hydrogen or a non-hydrogen substituent

p is the mole fraction of the fused oxygen ring units based on total units in polymer; and r is the mole fraction of the fused optionally substituted norbornene units based on total units in the polymer, and p and r are each greater than zero.

21. The photoresist of claim 1 wherein the polymer comprises a structure the following Formula IVB:



wherein each Z' is oxygen, sulfur or carbon; m' is 1, 2, 3 or 4;

Q represents an optionally substituted carbon alicyclic ring with two ring members being adjacent carbons of the polymer backbone;

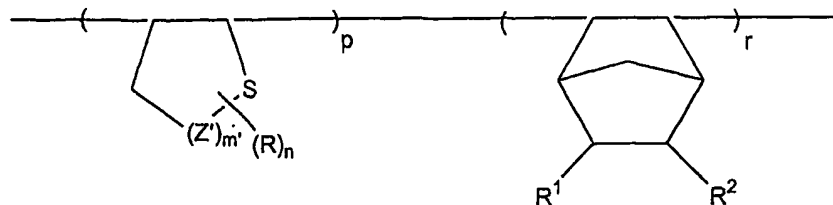
each R is the same or different non-hydrogen substituent;

n is an integer of from 0 to the maximum value permitted by the valences ring members;

p is the mole fraction of the fused oxygen ring units based on total units in polymer; and r is the mole fraction of the fused carbon alicyclic ring units based on units in the polymer, and p and r are each greater than zero.

22. The photoresist of claim 1 wherein the polymer comprises a structure the following Formula IVC:

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wherein Z' is oxygen, sulfur or carbon; m' is 1, 2, 3 or 4;
 each R is the same or different non-hydrogen substituent;
 n is an integer of from 0 to the maximum value substitution permitted by the valences of the ring members;
 R^1 and R^2 are each independently hydrogen or a non-hydrogen substituent
 p is the mole fraction of the fused oxygen ring units based on total units in polymer; and r is the mole fraction of the fused carbon alicyclic ring units based on units in the polymer, and p and r are each greater than zero.

23. The photoresist of any one of claims 1 through 22 wherein the polymer is a tetrapolymer or a pentapolymer.

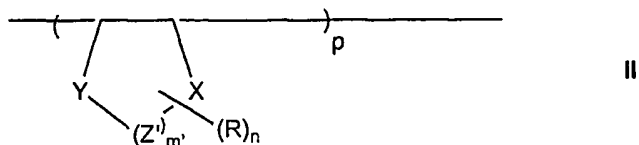
24. The photoresist of any one of claims 1 through 23 wherein the polymer is completely free of aromatic groups.

25. A photoresist composition comprising a photoactive component and a polymer that comprises i) a heteroalicyclic group that contains one or more sulfur members; and ii) a photoacid-labile moiety.

26. The photoresist of claim 25 wherein the photoacid-labile moiety is a polymer unit separate from the heteroalicyclic group.

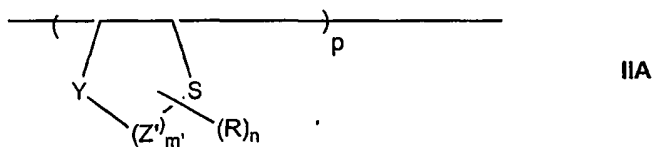
27. The photoresist of claim 25 wherein the polymer comprises a polyacrylate that comprises a photoacid-labile moiety.

28. The photoresist of claim 25 wherein the polymer contains units of following Formula II:



wherein X, Y, and each Z are each independently carbon, oxygen or sulfur; at least one of X, Y or Z being sulfur; each R is the same or different non-hydrogen substituent; m is 1, 2, 3 or 4; n is an integer of 0 to the maximum value permitted by the valences of the ring members; and p is greater than zero and is the mole percent of units in the polymer.

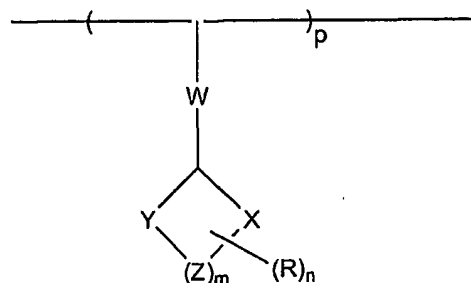
29. The photoresist of claim 25 wherein the polymer contains units of following Formula IIA:



wherein Y and Z' are each independently carbon, oxygen or sulfur; m' is 1, 2, 3 or 4; each R is the same or different non-hydrogen substituent; n is an integer of 0 to the maximum value permitted by the valences of the ring members; and p is greater than zero and is the mole percent of the units in the polymer.

30. The photoresist of claim 25 wherein the polymer comprises units of following Formula III:

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III

wherein W is a linker;

wherein X, Y, and each Z are each independently carbon, oxygen, or sulfur, at least one of X, Y or Z being oxygen or sulfur;

each R is the same or different non-hydrogen substituent;

m is 1, 2, 3, 4 or 5; n is an integer of from 0 to the maximum value substituted permitted by the valences of the ring members; and p is greater than zero and is the percent of the units in the polymer.

31. The photoresist of any one of claims 25 through 30 wherein the photoresist further comprises one or more units selected from the group consisting of carbon alicyclic, lactone, and anhydride.

32. The photoresist of any one of claims 25 through 31 wherein the photoresist comprises norbornene units.

33. The photoresist of any one of claims 25 through 32 wherein the photoresist is a tetrapolymer or a pentapolymer.

34. The photoresist of any one of claims 25 through 33 wherein the photoresist is completely free of aromatic groups.

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35. A method of forming a positive photoresist relief image, comprising
- (a) applying a coating layer of a photoresist of any one of claims 1 through 34 on a substrate; and
 - (b) exposing and developing the photoresist layer to yield a relief image.

36. The method of claim 35 wherein the photoresist layer is exposed to radiation having a wavelength of less than about 200 nm.

37. The method of claim 35 wherein the photoresist layer is exposed to radiation having a wavelength of about 193 nm.

38. A method of forming a positive photoresist relief image, comprising
- (a) applying a coating layer of a photoresist of any one of claims 25 through 34 on a substrate; and
 - (b) exposing and developing the photoresist layer to yield a relief image.

39. The method of claim 38 wherein the photoresist layer is exposed to radiation having a wavelength of less than about 200 nm.

40. The method of claim 38 wherein the photoresist layer is exposed to radiation having a wavelength of about 193 nm.

41. An article of manufacture comprising a microelectronic wafer substrate having coated thereon a layer of the photoresist composition of any one of claims 1 through 24.

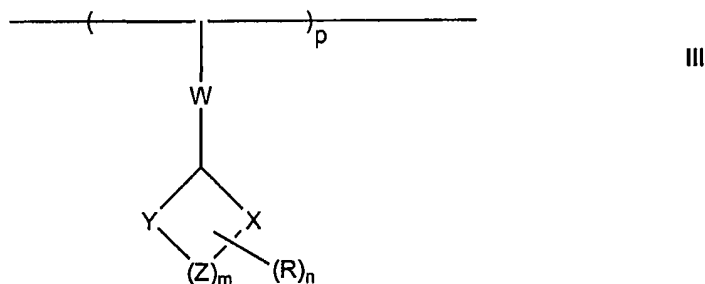
42. An article of manufacture comprising a microelectronic wafer substrate having coated thereon a layer of the photoresist composition of any one of claims 25 through 34.

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43. A polymer that comprises: i) a heteroalicyclic group fused to the polymer backbone and that contains one or more oxygen or sulfur ring members; ii) a heteroalicyclic group fused to the polymer backbone; and iii) a photoacid-labile moiety

44. A polymer that comprises: i) a heteroalicyclic group that contains one or more sulfur ring members; and ii) a photoacid-labile group.

45. A polymer that comprises units of the following Formula III:



wherein W is a linker;

wherein X, Y, and each Z are each independently carbon, oxygen, or sulfur; at least one of X, Y or Z being oxygen or sulfur;

each R is the same or different non-hydrogen substituent;

m is 1, 2, 4 or 5; n is an integer of from 0 to the maximum value substituent permitted by the valences of the ring members; and p is the mole percent of the unit in the polymer.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US01/14914

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) :G03F 7/039

US CL :430/270.1

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 430/270.1; 526/256, 257, 266, 267, 270, 271, 272

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Please See Extra Sheet.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 2,320,718 A (JUNG et al) 01 July 1998, Example VII, pages 2-3.	1-2, 4/1, 4/2, 14-15
X	EP 0,836,119 A1 (YOOL et al) 15 April 1998, Abstract and Examples.	1-2, 4/1, 4/2, 14-15
X, P	US 6,146,810 A (SEO et al) 14 November 2000, Detailed Description of the Invention, col. 4, Examples, Claims.	1-2, 4/1, 4/2, 14-15
X, P	US 6,150,069 A (JUNG et al) 21 November 2000, col. 2, lines 6-61, col. 3, lines 1 through col. 6, lines 37, Examples.	1-2, 4/1, 4/2, 14-15
X,P	US 6,143,472 A (SUMINO et al) 07 November 2000, third, fourth and sixth terpolymer in col. 23.	1-2, 4/1, 4/2, 14-15,18

☒ Further documents are listed in the continuation of Box C.
 ☐ See patent family annex.

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier document published on or after the international filing date	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Z" document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

26 JUNE 2001

Date of mailing of the international search report

22 AUG 2001

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US01/14914

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5,843,624 A (HOULIHAN et al) 01 December 1998, Abstract, Figures, Examples 7 and 9.	1-2, 4/1, 4/2, 14-15

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US01/14914

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☒ Claims Nos.: 5-13, 23-24, 32-42
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

Please See Extra Sheet.

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:
1-4, 14-22

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US01/14914

B. FIELDS SEARCHED

Electronic data bases consulted (Name of data base and where practicable terms used):

EAST (USPAT file)

search terms: 430/270.1, 526/256, 526/257, 526/266, 526/267, 526/270, 526/271, 526/272, fused, sulfur, sulphur, heterocyclic, anhydride

BOX II. OBSERVATIONS WHERE UNITY OF INVENTION WAS LACKING

This ISA found multiple inventions as follows:

This application contains the following inventions or groups of inventions which are not so linked as to form a single inventive concept under PCT Rule 13.1. In order for all inventions to be searched, the appropriate additional search fees must be paid.

Group I, claim(s) 1-4, 14-22, drawn to a photoresist composition comprising a photoactive component and a polymer comprising a heterocyclic group fused to the polymer backbone and that contains one or more oxygen or sulfur ring members and a photoacid-labile moiety.

Group II, claim(s) 43, drawn to a polymer comprising a heterocyclic group fused to the polymer backbone and that contains one or more oxygen or sulfur ring members and a photoacid-labile moiety.

Group III, claim(s) 25-31, 44, drawn to (1) a photoresist composition comprising a photoactive component and a polymer that comprises a heterocyclic group that contains one or more sulfur ring members and a photoacid labile moiety and (2) a polymer that comprises a heterocyclic group that contains one or more sulfur ring members and a photoacid labile group.

Group IV, claim(s) 45, drawn to a polymer comprised of specified Formula III wherein no limitation of the presence of a photoacid-labile moiety, or a heterocyclic group fused to a polymer backbone, or a carbon alicyclic group fused to the polymer backbone is made.

The inventions listed as Groups I, II and III do not relate to a single inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons: Claim 1 is anticipated by Jung et al (GB 2320718A) as shown in Example VII and in composition attributed to AT and T (or Bell Laboratory) on pages 2-3 present compositions which anticipate the instant composition wherein Jung et al the fused heterocyclic group is a cyclic anhydride with an oxygen in the ring or the carbonate of Formula IV in claim 1. The t-butyl group is the photoacid labile moiety. Claim 1 is anticipated by Yool et al (EP 0 896 119 A1) in their examples wherein the copolymers and terpolymers and their chemically amplified compositions wherein a cyclic anhydride is the fused heterocyclic structure with oxygen being the non carbon present in the ring. Consequently the special technical feature which links Groups I and II, ie a photoresist composition comprising a photoreactive component and a polymer that comprises a heterocyclic group that contains one or more oxygen or sulfur ring members and a photoacid-labile moiety, does not provide a contribution over the prior art, so unity of invention is lacking. With respect to Group I and Group III, the same reasoning with respect to lack of unity is true as is for the separation of Group II and III, since Jung et al and Yool et al would anticipate the polymer of claim 43 in Group II.

The inventions listed as Groups I and IV do not relate to a single inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons: The special technical feature linking Group I to Group IV is a polymer comprised of a heterocyclic ring containing an oxygen or sulfur ring. Since Group IV requires said ring be fused to the polymer backbone and the heterocyclic ring of Group IV has no such requirement only the presence of a polymer with an oxygen or sulfur ring atom unites these two inventions. Jung et al and Yool et al anticipate the presence of such a polymer with an oxygen atom with respect to the polymer of Group I. Thus, the special technical feature which links Groups I and IV does not provide a contribution over the prior art, so unity of invention is lacking.

The inventions listed as Groups IV and III do not relate to a single inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons: The special technical feature linking Group IV and III is a polymer comprising a heterocyclic group that contains an oxygen or sulfur atom. Jung et al and Yool et al teach this aspect in the prior art thus anticipate the special technical feature that unites these two Groups. Thus, the special technical feature which links Groups III and IV does not provide a contribution over the prior art, so unity of invention is lacking.